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“Computational Modeling of Actinide Complexes”

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We will present our recent studies on computational actinide chemistry of complexes which are not only interesting from the standpoint of actinide coordination chemistry but also of relevance to environmental management of high-level nuclear wastes. We will be discussing our recent collaborative efforts with Professor Heino Nitsche of LBNL whose research group has been actively carrying out experimental studies on these species. Computations of actinide complexes are also quintessential to our understanding of the complexes found in geochemical, biochemical environments and actinide chemistry relevant to advanced nuclear systems. In particular we have been studying uranyl, plutonyl, and Cm(III) complexes in aqueous solution. These studies are made with a variety of relativistic methods such as coupled cluster methods, DFT, and complete active space multi-configuration self-consistent-field (CASSCF) followed by large-scale CI computations and relativistic CI (RCI) computations up to 60 million configurations.

Our computational studies on actinide complexes were motivated by ongoing EXAFS studies of speciated complexes in geo and biochemical environments carried out by Prof Heino Nitsche's group at Berkeley, Dr. David Clark at Los Alamos and Dr. Gibson's work on small actinide molecules at ORNL. The hydrolysis reactions of uranyl, neptunyl and plutonyl complexes have received considerable attention due to their geochemical and biochemical importance but the results of free energies in solution and the mechanism of deprotonation have been topic of considerable uncertainty. We have computed deprotonating and migration of one water molecule from the first solvation shell to the second shell in $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$, $\text{UO}_2(\text{H}_2\text{O})_5^{2+}\text{NpO}_2(\text{H}_2\text{O})_6^+$, and $\text{PuO}_2(\text{H}_2\text{O})_5^{2+}$ complexes. Our computed Gibbs free energy (7.27 kcal/m) in solution for the first time agrees with the experiment (7.1 kcal/m) while previous computations produced results in strong disagreement. We have studied the electronic and spectroscopic properties of plutonyl carbonate complexes of the types $\text{PuO}_2\text{CO}_3 \cdot n\text{H}_2\text{O}$, ($n=1,2$) and $\text{PuO}_2(\text{CO}_3)_3\text{Ca}_3$. Our computed equilibrium geometries and vibrational spectra of these species agree quite well with the EXAFS. Recent results on Cm(III) complexes with ligands that have multiple binding capabilities will be compared with experiment.

References

1. D. Majumdar and K. Balasubramanian, “Theoretical studies on uranyl–silicate, uranyl–phosphate and uranyl–arsenate interactions in the model $\text{H}_2\text{UO}_2\text{SiO}_4 \cdot 3\text{H}_2\text{O}$, $\text{HUO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{HUO}_2\text{AsO}_4 \cdot 3\text{H}_2\text{O}$ molecules”, *Chemical Physics Letters*, **397**, 26-33 (2004).
2. Z. Cao and K. Balasubramanian, “Theoretical Studies of hydrated complexes of uranyl, neptunyl and plutonyl in aqueous solution: $\text{UO}_2^{2+}(\text{H}_2\text{O})_n$, $\text{NpO}_2^{2+}(\text{H}_2\text{O})_n$, and $\text{PuO}_2^{2+}(\text{H}_2\text{O})_n$ ”, *J. Chem. Phys.* **123**, 114309-1 to 114309-12 (2005)

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